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Unsaturated polyester resins from glycolysed waste polyethyleneterephthalate: synthesis and comparison of properties and performance with virgin resin

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Recycling of polyethyleneterephthalate (PET) bottles for soft drinks is accomplished by depolymerization through glycolysis. Obtained intermediates are reacted with mixtures of saturated and unsaturated acids to obtain unsaturated polyesters (UP) suitable for use as a matrix for fibre-reinforced thermosetting composites. The influence of chemical structure of glycols on the chemo-rheological behaviour of resins, has been verified. By using di-ethylene glycol, the behaviour of the resulting UP closely resembles that of UP obtained from virgin monomers. Moreover, composite sheets containing UP developed in the present research, show enhanced toughness if compared with the analogous composite made of virgin UP resin.

1. Introduction

Polyethylene terephthalate (PET) is a semicrystalline thermoplastic used, for example, in the manufacture of high-strength fibres, photographic films and soft-drink bottles. In Italy in 1989 the volume of PET consumed in the beverage industry was more than 90 thousand tons, corresponding to more than 9.5 million bottles. The disposal of these large numbers of bottles and of urban plastic waste and their environmental impact have prompted the Italian Government to impose a mandatory recycling law, the 475-88, for post-consumer plastics, and to found the Mandatory National Consortium for the Recycle for Plastic Containers for Liquids, REPLASTIC. PET bottles have become one of most valuable recyclable materials today. However, to sustain an economically viable recycling programme, secondary end-use applications of the reclaimed PET must be developed. In addition to mechanical methods of reusing plastics, PET can be reclaimed by chemical means and used to produce new polymer compositions.

The various possibilities for utilizing PET product waste have been studied for many years [1–4]. In our laboratory, we are investigating the depolymerization of recycled PET into its monomers and higher oligomers. The intermediates thus obtained can then be used as building blocks to synthesise other polymers with higher economical values. Of particular interest is the realization of long-lasting items; in such a way we transform a disposable plastic into a durable object, with evident relief of the environmental pressure. The system studied in the present work was the preparation of unsaturated polyesters as a matrix for composites starting from the depolymerized PET bottle.

The unsaturated polyester (UP) resins are used extensively as a matrix for fibre-reinforced plastics (FRP), which are replacing conventional structural materials. The widespread use of UP resins in FRP is due to their low cost and the wide variety of grades available to meet specific property requirements. The UP resins are made by reaction of aliphatic diols with unsaturated and saturated diacids. The proper selection of monomers is governed by the desired combination of properties in the final product.

In the present investigation, the PET recycled from post-consumer soft-drink bottles was depolymerized by glycolysis in excess di-ethylene glycol (DEG). The glycolysed product was used to synthesize UP resin, which was then used as matrix in FRP. The objective of this study was to evaluate the characteristics of FRP obtained from PET waste and to compare its properties with those of the general purpose FRP.

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2. Experimental procedure

2.1. Glycolysis of PET waste

PET waste flakes, totalling 800 g, equivalent to 4.2 mol repeating unit (mol. wt. 192), were added to 1200 g DEG (mol. wt. 106), such that the molar ratio of PET repeating unit to DEG was 1 : 2.7. The mixture was charged into a four-necked round-bottom flask, which was fitted with stirrer, reflux condenser, nitrogen inlet and thermometer. The reactor was immersed in an oil bath and the temperature was brought up to 220 °C. The glycolysis reaction was allowed to proceed for up to 12 h, with small samples removed periodically to monitor the progress of the reaction. In order to check the extent of depolymerization, the glycolysed products were analysed for hydroxyl and acid values.

The hydroxyl values were evaluated according to ASTM D2849 Method A. About 0.5 g sample was accurately weighed and added to 10 ml acetylating solution, containing 88 : 12 (vol/vol) pyridine and acetic anhydride, in a 50 ml round-bottomed flask. The flask was fitted with a vertical reflux condenser and heated with stirring in a boiling water bath for about 2 h. The mixture was then cooled to room temperature and hydrolysed by 100 ml chilled distilled water in another flask. Under vigorous stirring, 20 ml benzene were added. The resulting solution was titrated against 0.5 N KOH standard using phenolphthalein as indicator. A blank run, i.e. without the sample, was also performed.

Measurement of the acid value gave a direct guide to the number of terminal carboxyl groups and therefore to the degree of reaction that had taken place. The acid value was determined by titrating the mixture of a weighed amount of sample in 100 ml solution, containing 2 : 1 (vol/vol) toluene and ethanol, against 0.2 N standard KOH using phenolphthalein indicator.

2.2. Preparation of the unsaturated polyester

The UP resin was prepared by reacting the glycolysed products with maleic anhydride (AM) and phthalic anhydride (AF) at a fixed ratio of 1 : 1 for the hydroxyl-to-carboxyl groups. The hydroxyl number of the glycolysed products was used for computing the amount of anhydrides, whose molar ratio for AM to AF was 80 : 20. Thus the UP resin was synthesized by reacting 1996 g glycolysed products with 930 g AM and 361 g AF. About 10% xylol was added as solvent, to help the removal of water by-product through azeotropic distillation. The reaction was carried out in a 5 l round-bottom flask having a distillation condenser, a thermowell, a gas bubbler and stirring assembly. In the reflux line from the flask a Dean and Stark type trap was used so that the heterogeneous condensate could be separated automatically into its two phases. In this way the solvent was returned to the flask, leaving the water behind which could be measured. The reactants were heated from 140 °C to 210 °C, then the temperature was held at 210 °C until the acid value reached about 60. At the end of the reaction, the solvent was distilled off. The liquid resin was cooled to 120 °C and 100 p.p.m. hydroquinone was added. The UP resin was dissolved in styrene monomer at 70 °C to obtain 40% (wt/wt) styrene in the final resin. This resin was coded UPE-DEG. The unsaturated polyester resin was analysed for hydroxyl and acid values; these were, respectively, 670 and 6.7.

The processing characteristics such as viscosity, gel time and exothermicity of the resin were investigated. The viscosity measurements were carried out in a constant temperature bath at 25 °C using a Brookfield viscometer. The gel time, t_g, and peak exotherm, t_p, were determined using 1% MEKP as the initiator and 0.05% (wt/wt) cobalt octoate as the accelerator. A general purpose resin (provided by Lonza S.p.A.), containing AM, AF, DEG and PG, was used as the reference resin, labelled A.

2.3. Preparation of the cured resin

The resins were cast in a glass cell composed of two vertical sheets glass, separated by a neoprene gasket, held together with G-clamps. 1% MEKP was used as the catalyst and 0.05% cobalt octoate as the accelerator. The resins sheets were kept for 12 h in a water bath at 70 °C and then post-cured at 100 °C for 2 h.

2.4. Preparation of the fibre-reinforced plastic

The glass fibre-reinforced laminates were manufactured by Lonza S.p.A., according to their operating conditions. The resin we synthesized, UPE- DEG, and the reference resin A, were used as matrix in a contact moulding process. The resulting laminates were coded FRP-DEG and FRP-A. Three fibre glass mats were impregnated by hand in successive plies, with catalysed UP resin (1.5% MEKP, 0.2% Co-oct). The laminates were cast at room temperature for 24 h in a glass cell similar to that used to cure the resin. Then they were post-cured at 100 °C for 2 h and then another hour without clamps, to bring the laminates to a stable condition.

2.5. Testing

Calorimetric measurements were taken with a Mettler TA-3000 apparatus, equipped with a control and programming unit (microprocessor TC 10) and a calorimetric cell DSC 30, that allows a temperature scan from − 170–600 °C, to determine the heat related to the curing and to study the kinetics of the process. Two different catalytic systems were used: 1% MEKP without accelerator or with 0.05% cobalt octoate. Samples were rapidly cooled to − 100 °C and then heated to 250 °C using a scan rate of 10 deg min^{-1}. A second heating cycle was operated, after having cooled the resin to −50 °C, from −50 °C to 200 °C at a scan rate of 20 deg min^{-1}.

Dynamical mechanical thermal analysis (DMTA) was used to measure the glass transition, T_g, and the loss of rigidity. The installation was a PL-DMTA Mk III consisting of a dynamic mechanical thermal analyser unit, a temperature programmer, an electromechanical measurement unit, and a computer controller. Measurements were made in flexural geometry, at a constant frequency of 10 Hz with an imposed strain of 32 μ, heating the sample from -50–250 °C at a rate of 3 deg min^{-1}. Specimens were 1 mm × 5 mm × 10 mm beams cut from sheets of cured resin.

A compression test was conducted according ASTM D 695-80. The test machine was an Instron type 1122, comprising a drive mechanism, a load indicator and a compressometer. Test specimens were beams, machined from flat cast sheets of resin, whose sizes were 3.5 mm × 4.5 mm × 6 mm; five specimens for each sample were tested. The compression load was applied at a rate of 1 mm min^{-1}.

Flexural properties were performed according to ASTM D 790-81 method I, for cured resins. The testing machine was the Instron type 1122 used for compression tests with different loading noses and supports. Test specimens were beams sized 6 mm × 4.5 mm × 70 mm, with a notch midway along the larger dimension of the specimens' cross-section, 2 mm deep. Five specimens for each sample were tested. The rate of loading motion was 1 mm min^{-1}.

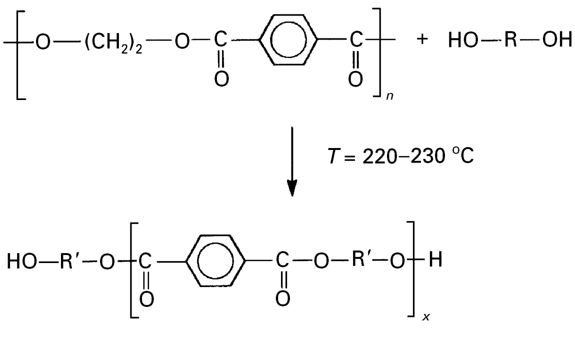
A Charpy type test was performed according to ASTM D 256-81 to evaluate the impact resistance of cured resins. Test specimens were notched prisms like those of the flexural test.

The flexural and tensile properties of FRP were determined following the specification of ISO 178:93 and ISO 527/1-2:93. The fracture surfaces of all the specimens of cured resin and FRP samples were studied by scanning electron microscopy (SEM). The morphological properties of polymer surfaces were analysed by means of the topographic images yielded by SEM. A Philips SEM 501 was used to scan the fracture surfaces.

3. Results and discussion

3.1. Glycolysis of PET waste

PET is commonly synthesised either by reacting terephthalic acid (TPA) and ethylene glycol (EG), or dimethyl terephthalate and EG. Then, when the chains of PET are broken down, these fragments can be found.



(1)

where R = R' in case of EG is used for depolymerization, while R ≠ R' when a glycol other than EG is used.

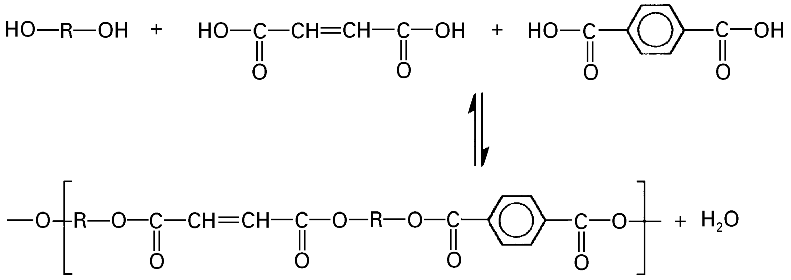
The choice of DEG to carry out the glycolysis has been determined by the necessity of having good flexural properties in the UP resin, because of its use as a matrix in FRP. The long chain of the glycol improves flexibility in the final cured resin, but the oxygen linkages reduce the styrene compatibility [5].

Two other glycolysis systems were performed, one with di-propylene glycol (DPG) and the other with equimolar ratio of DEG and PG, to increase the compatibility with styrene; the results will be analysed later.

The major fractions of the glycolysed product by the DEG glycolysis could be represented by the following species: DEG-TPA-DEG, EG-TPA-DEG, EG-TPA-EG, DEG and a small amount of EG.

3.2. Polyesterification

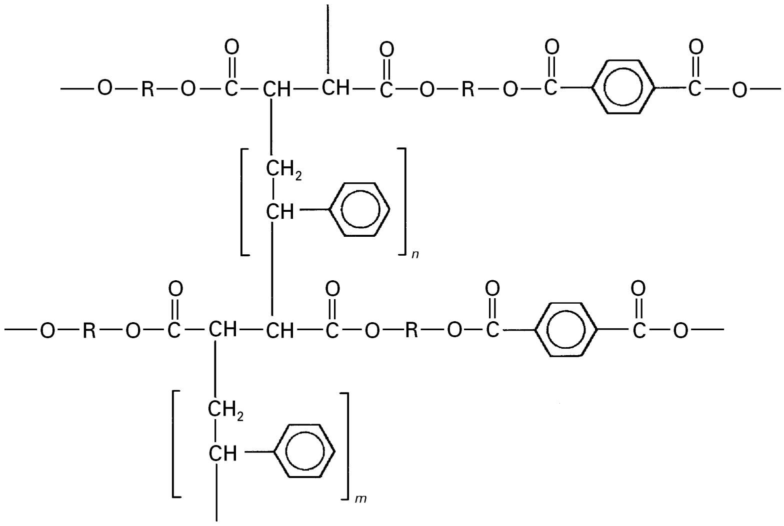
The glycolysed products were polyesterified with AM and AF. The polyesterification is a reversible step-growth reaction. The polymer is produced with the evolution of water



(2)

It is possible to carry out the reaction in the presence of a solvent such as xylene that greatly accelerates the polycondensation because the water is removed more rapidly. Many studies of the kinetics of the reaction have been made [2, 3].

The reactivity of the unsaturated polyester polymer towards the cross-linking reaction was derived primarily from the maleic anhydride component. More AF was also added to reduce the degree of unsaturation and hence to reduce the danger of a too short gel time that could adversely affect the processability of the resin. To regulate the cross-linking reaction, styrene monomer was incorporated as cross-linking agent. The content of styrene in the final resin is important to ensure good processability. Moreover, it must be checked accurately because we can have high shrinkage on curing or a tendency not to cure fully, with high or low content, respectively [5]. To prevent premature gelation and to inhibit the spontaneous polymerization of the resin, hydroquinone was added. This solution was cured to a thermoset cross-linked polymer by a process of polyaddition with the aid of an initiator and an activator, as described earlier (see scheme I below). The various steps in a polyester polymerization are typical of free-radical catalysed polymerization systems.



(I) Structure of thermoset cross-linked UPE.

When the polyesterification reactions were carried out with the UPE products obtained from DPG or DEG-PG glycolysis, a two-phase polyester was produced, one phase of which was incompatible with styrene. In fact, the rate of polycondensation was influenced by the structure of the glycols [6]. Branched glycols, such as DPG and PG, because of their steric hindrance, are less reactive towards AM than other oligomers and glycols in the reaction mass. At the end of polyesterification, we have different polymeric chains produced by combination of the glycolysed products with anhydrides, but also unreacted oligomers with pendant methyl grouping and excess AM that form the phase which is insoluble in styrene. Then, this phase will not take part in cross-linking while the remaining UPE will be dissolved in excess styrene, and hence the gelation will be strongly delayed. In addition it contains short chains not incorporated into the network, so it can act as plasticizer in the cured resin, reducing its hardness. Thus, resins obtained from glycolysis with DPG and PG did not have optimum properties to manufacture FRP.

The results of the characterization of the UPE-DEG resin and of the reference resin A are given in Table I and Fig. 1. Processing characteristics of the PET-based resin are comparable with those of the A resin, therefore the flow behaviour during moulding will be similar.

The curing kinetics of UP resins have been investigated using differential scanning calorimetry (DSC), carrying out isothermal and non-isothermal experiments [7, 8]. DSC provides information is useful in selecting and optimizing accelerator amounts in a catalytic system and the reactivity and efficiency of these systems in the free-radical polymerization of UP resin and reactive monomer can be evaluated. From the DSC measurements, the heat flow generated during the exothermic chemical reaction of curing can be monitored, and the overall heat of the curing process is found to be the resultant of more than one reaction [7]. Moreover, it is assumed that the reaction rate is directly proportional to the heat generation, ΔH, and that the heat generated by a chemical reaction is proportional to the extent of the reaction. The kinetic parameters are determined from the exothermal peak obtained from isothermal and non-isothermal measurements. From non-isothermal curing experiments, various information is obtained, as reported in Table II: the temperature at which the reaction begins, T_{in}, and ends, T_{fin}; the value of temperature at which an exothermic peak occurs, T_1 and T_2; the amount of heat generated by the curing reaction, ΔH.

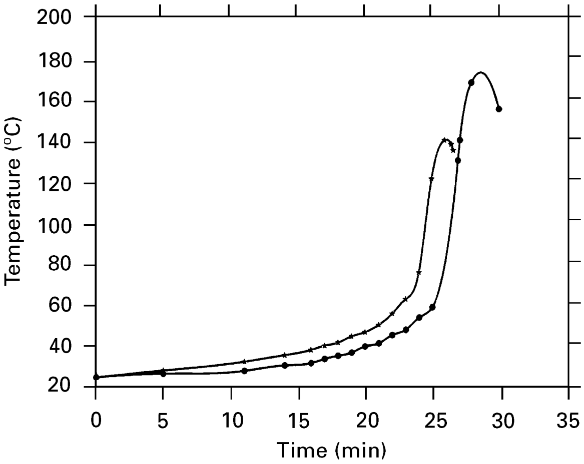


Figure 1 Gelation time versus temperature. (★) A, 0.05% Co-oct at $T = 140\,^{\circ}\mathrm{C}$; (●) UPE-DEG, 0.05% Co-oct at $T = 168\,^{\circ}\mathrm{C}$.

TABLE I Characterization of unsaturated polyester resins

	Hydroxyl value	Acid value	Viscosity (mPas)	Gel time (min)	Peak exotherm (min)
UPE-DEG	74.5	24	290	14	28
A	38	25	300	11	26

TABLE II Summary of parameters evaluated from DSC

	T_{in} (°C)	T_1 (°C)	T_2 (°C)	T_{fin} (°C)	ΔH (J g^{-1})	n	E_a (kJ mol^{-1})	Ln k_0
A 0%	73	111		214	261	2.96	188	55
A 0.05%	49	91		213	289	1.96	90	25.5
UPE-DEG 0%	72	117		177	242	1.89	155	44
UPE-DEG 0.025%	40	90	110	170	293	1.53	65	16
UPE-DEG 0.05%	36	85	104	170	292	1.66	66	17

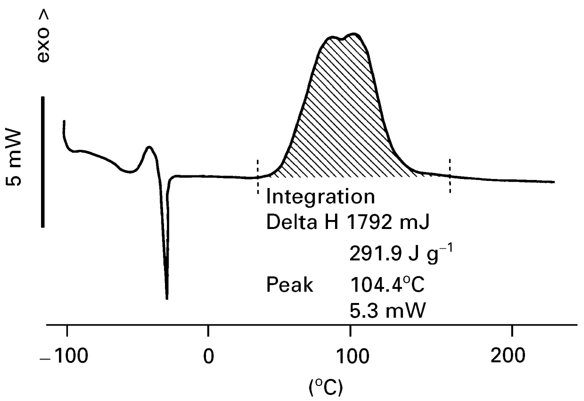


Figure 2 DSC plot of UPE-DEG with 0.05% Co-oct (I run) (for details, see text).

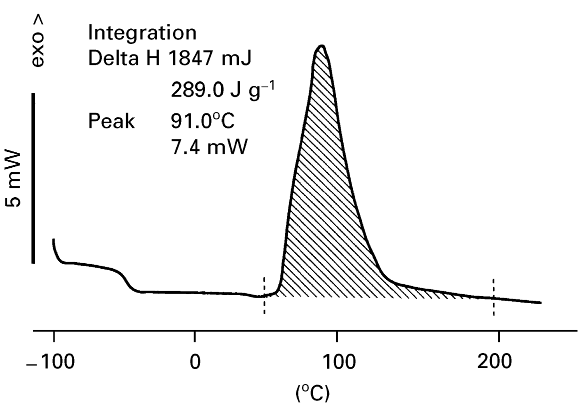


Figure 3 DSC plot of A with 0.05% Co-oct (I run) (for details, see text).

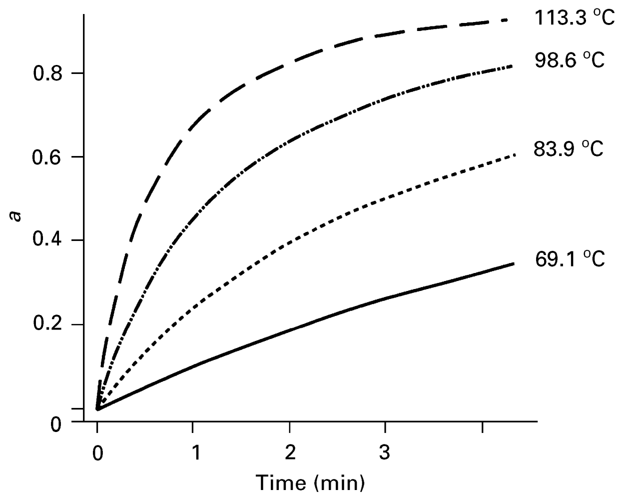


Figure 4 Reaction plot (reaction conversion, *a*, versus time) of UPE-DEG with 0.05% Co-oct (I run)

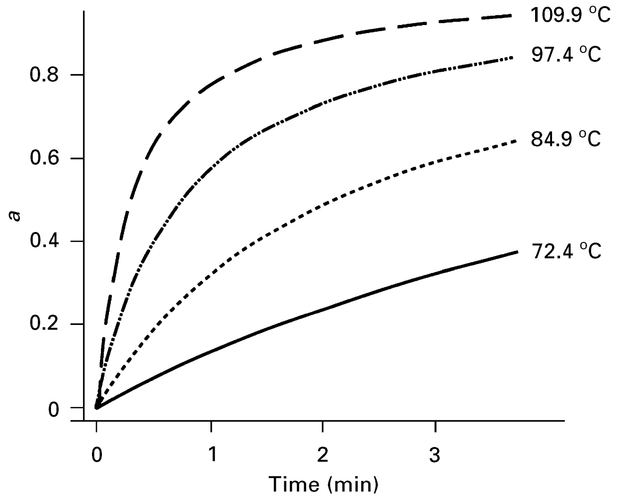


Figure 5 Reaction plot (reaction conversion, *a*, versus time) of A with 0.05% Co-oct (I run).

Figs 2 and 3 show plots of ΔH versus cure temperature. The coded UPE-DEG 0% or UPE-DEG 0.05% are systems in which the resin is catalysed with 1% MEKP and 0% or 0.05% cobalt octoate, respectively. The temperature at which the reaction starts decreases with increasing amount of accelerator, as well as the temperature at which an exothermic peak occurs, whereas the size of this peak increases with the amount of cobalt octoate. Moreover, these values for UPE-DEG are very close to those of the reference resin A, indicating that the behaviour of the curing process is similar.

The rate of the curing reaction increases with the amount of the accelerator, as confirmed by the kinetic parameters: E_a is the activation energy, n a constant describing the order of the reaction, and k_0 is the rate constant. Figs 4 and 5 show the reaction conversion, *a*, versus time at different temperatures, from which the degree of cure reaction can be evaluated after a determinated reaction time.

UPE-DEG with accelerator exhibits two exothermic peaks, whereas the resin without accelerator shows only a single exothermic peak. The existence of two peaks suggests that two initiation reactions occur in the UP resin containing MEKP as initiator and cobalt octoate as promoter. The second exothermic peak of the resin containing promoter corresponds to the single peak without promoter, as indicated by previous studies [7, 8].

The second heating cycle was carried out to check that the cure reaction had been completed during the first run and thus that the cast resin was in a stable condition. It is evident that no residual heat had evolved from the sample.

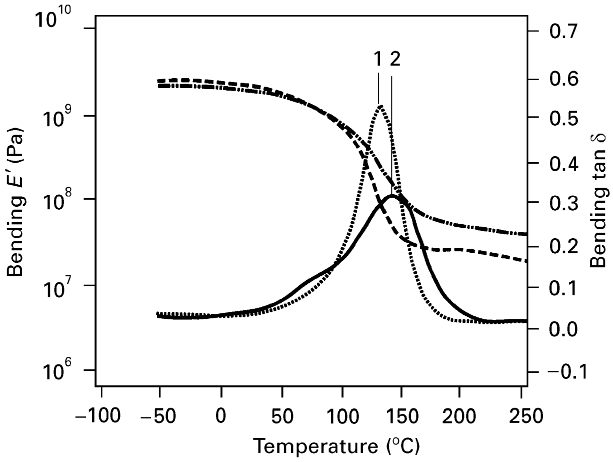


Figure 6 DMTA plot of (– – –, ●) UPE-DEG and (– · · –, —) A, for (– – –, – – · · – –) E' and (●, —) tan δ, with 0.05% Co-oct. Peak 1, 132.30 °C; peak 2, 142.42 °C.

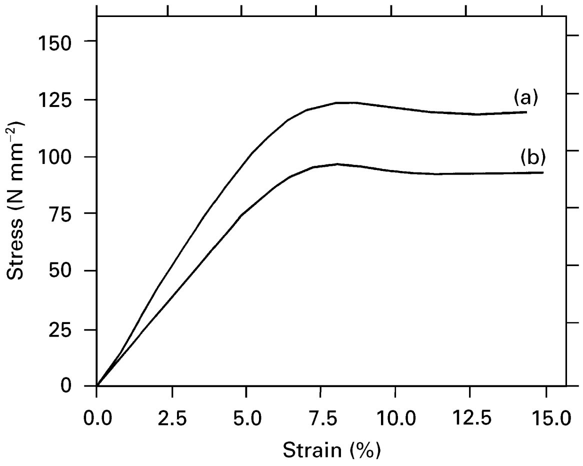


Figure 7 Stress–strain diagram of (a) A and (b) UPE-DEG with 0.05% Co-oct.

Dynamic mechanical testing is a useful characterization technique for polymers. Because a periodic load is applied, the time-dependence of the resultant strain can be measured exactly with respect to the applied stress. DMTA enables a full exploration of relaxational mechanisms present in viscoelastic materials. As such, it is a very sensitive means of measuring the glass transition, T_g.

A flexural geometry of testing was chosen because it is more suitable for brittle materials, like thermosetting polyesters. A sinusoidal load was applied to the sample and the real, E', and imaginary, E'', moduli were measured. The real and imaginary moduli represent the elastic and viscous behaviour of the sample, respectively. Their ratio E''/E' defines the loss tangent or damping tan δ. When loading the sample during the heating process, a transition from a semi-crystalline network to the rubbery state occurs and a maximum in the damping tan δ and a drop of the elastic modulus, E', will appear in the DMTA plot. In Fig. 6 the DMTA plot for UPE-DEG and A resins catalysed with 1% initiator and 0.05% promoter is shown. The outlines of the curves are analogous and T_g values show small difference. The T_g is strictly related to mechanical properties, such as impact resistance, toughness, loss of rigidity and relaxation. In particular, polymers which show a high impact resistance at room temperature have major peaks of loss of rigidity at low temperature.

Unmodified, cured, unsaturated polyester resins have low strength and are prone to stress cracking and brittle fracture. In structural applications, reinforcing fibres improve tensile, compression and impact strengths. A high modulus of elasticity is also possible [5]. Fig. 7 reports the stress–strain behaviour in compression tests. In comparison with tension, compression test have their advantages when performed on brittle materials [9]. A stress–strain diagram is used to find modulus of elasticity, E, yield stress, σ_y, deformation at yield point, ε_y%, ultimate stress, σ_r, and relative elongation at failure, ε_r%. However, brittle materials lend themselves to difficult compression tests. For this reason, bending tests are also used to assess their deformation and strength characteristics. As in bending, Charpy test notched specimens were used. These two tests utilize a three-point loading system and bring specimens to rupture. The main difference between them is the rate at which the load is applied to specimens, directly opposite the notch which acts as stress concentrator. The stress concentration promotes a brittle rather than a ductile fracture. To study the fracture of rigid polymers, fracture mechanics can be applied. This theory has received considerable attention [10]. Two main, interrelatable, conditions for fracture are proposed [10]. An energetic approach provides a measure of the fracture energy, G_c, required to extend a crack over unit area. A second approach refers to a stress intensity factor, K, and states that fracture occurs when the value of K exceeds some critical value K_c. K_c is a measure of a material property, often referred to as the material toughness. A basic aim of the fracture mechanics is to identify fracture criteria such as G_c and K_c. From the theoretical development of this theory, expressions to calculate the latter parameters are provided [10]. The concepts of linear elastic fracture mechanics may be applied also to polymers, even if the most brittle of polymers involves localized viscoelastic energy dissipative processes in the vicinity of the crack tip and then exhibits inelastic deformations, provided

TABLE III Compression properties

	σ_y (N mm^{-2})	ε_y (%)	σ_r (N mm^{-2})	ε_r (%)	E (MN m^{-2})
UPE-DEG	95.6	6.1	222.0	49.0	2422
A	122.3	5.9	176.3	39.8	2433

TABLE IV Results of the bending test

	F (N)	K_c (MN m$^{-3/2}$)	G_c (kJ m^{-2})
UPE-DEG	20.11	0.71	0.18
A	15.20	0.58	0.12

TABLE V Results of the Charpy test where F and U are the load and the energy to break test specimens

	F (N)	K_c (MN m$^{-3/2}$)	G_c (kJ m^{-2})	U (mJ)
UPE-DEG	21.61	0.77	0.29	4.10
A	16.13	0.63	0.15	1.78

TABLE VI Properties of fibre-reinforced plastics

	FRP-DEG	FRP-A
Tensile strength (MPa)	181	127
Tensile modulus (MPa)	10440	9700
Flexural strength (MPa)	317	242
Flexural modulus (MPa)	10110	9400

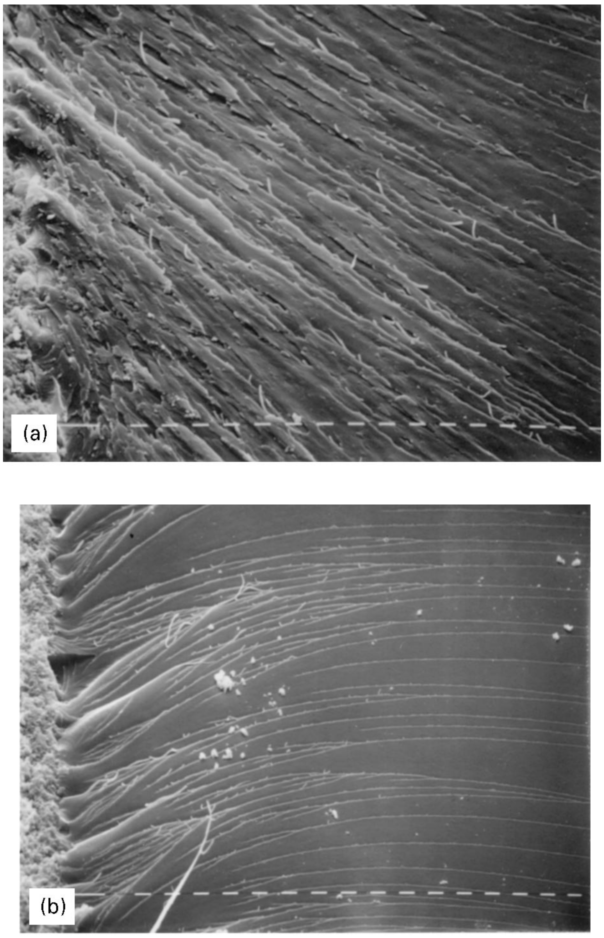


Figure 8 SEM images of the fracture surfaces of the flexural test specimens of (a) UPE-DEG and (b) A, with 0.05% Co-oct (×320).

that such deformations are confined around the tip.

Compression properties given in Table III show that UPE-DEG resin is more ductile than A resin, but it is also stronger at failure. Moreover UPE-DEG has good flexural characteristics (see Tables IV and V) which are improved by the long chain of DEG. The higher toughness of UPE-DEG is proved by K_c values in the table.

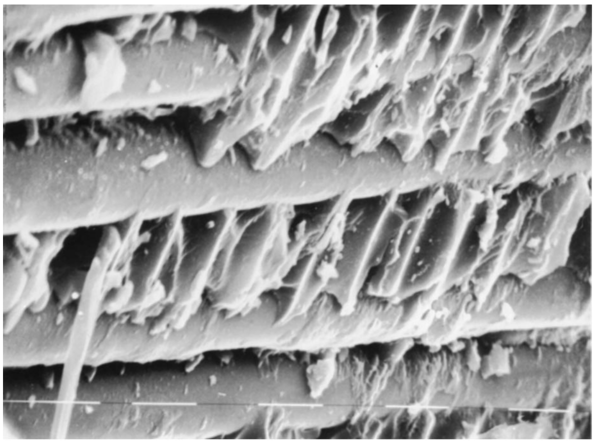


Figure 9 SEM image of the fracture surface of the tensile test specimen of FRP-DEG (×1250).

When UPE-DEG resin is used as a matrix in FRP, its tensile and flexural properties enhance the mechanical behaviour of the composite. Table VI shows the fundamental properties of FRP specimens. The values of tensile and flexural strengths are higher than those of the reference FRP; important improvements for the usual structural applications of the fibre-reinforced plastics.

SEM inspection confirms the previous discussion. Images of the fracture surfaces of the flexural test specimens (Fig. 8) show that in the UPE-DEG, the fracture lines are more marked and thicker than the lines of the reference resin, because of the improved tensile strength. Moreover, the propagation of fracture in UPE-DEG follows much more irregular paths, as a consequence of enhanced plastic deformation of the material.

Good adhesion along the resin–fibre boundary is recorded, as is evident from the analysis from Fig. 9.

Therefore, resins based on recycled PET allow optimum properties to be achieved in FRP manufacture, by the proper selection of the reacting monomers.

4. Conclusion

The objective of our investigation was to realize a process that allows the use of PET-based resins in value-added products. These PET-based resins would definitely benefit the FRP industries by offering versatility in processing and properties over conventional resins. In fact, recycled PET does not adversely affect the polymer composite properties and its use helps to reduce the cost of these products. In addition to the recycling of PET in FRP applications, it also allows energy saving and provides for a long-term disposal of the PET waste, an important consideration in recycling applications. A more precise balance is needed between costs of depolymerization and value addition. However, the costs to human beings by way of increased pollution may cover the possible shortfall.

References

1. S. BALIGA and W. T. WONG, *J. Polym. Sci., A Polym. Chem.* **27** (1989) 2071.
2. U. R. VAIDYA and V. M. NADKARNY, *J. Appl. Polym. Sci.* **34** (1988) 235.
3. *Idem*, *ibid.* **35** (1988) 775.
4. *Idem*, *Ind. Eng. Chem. Res.* **26** (1987) 194.
5. B. PARKIN, F. LAMB and B. V. CLIFTON, "Polyesters", Vol. 2 (The Plastics Institute, London, 1967).
6. J. Y. JADHAV and S. W. KANTOR, *Polyest. Unsat., Encycl. Polym. Sci. Eng.* **12** (1988) 156.
7. M. AVELLA, E. MARTUSCELLI and A. MAZZOLA, *J. Therm. Anal.* **30** (1985) 1359.
8. K. W. LEM and C. D. HAN, *Polym. Eng. Sci.* **24**(3) (1984) 174.
9. A. YA. MALKIN, A. A. ASKADSKY, V. V. KOVRIGA and A. E. CHALYKN, *Exp. Met. Polym. Phys.*, edited by A. Ya. Malkin (Moscow, 1983) pp. 11–60.
10. A. J. KINLOCH and R. J. YOUNG, "Fracture Behaviour of Polymers" (Applied Science, London, 1985) 74–106.

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